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Research and Application of a Novel Descaling and Anti-scaling Technology in Integrated Utilization of Geothermal Energy

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Abstract : Hot springs are very precious geothermal energy resources. Their three characteristics of "heat, mineral and water" make it great potential for integrated, comprehensive development with the primary, secondary and tertiary industries. Hot springs have a high medical value because they contain many trace minerals that benefit human health. However, one of the main problems in their applications is the scaling of conveying pipelines and systems. There are various ways of descaling processes in the market, but limited descaling techniques are available for consumer recreation sites such as hot springs, which require higher health concerns. This paper describes a new descaling and prevention process developed independently not to damage hot springs' water quality. Starting from the well, the problem of carbonate scaling in hot spring water is solved through comprehensive control of pressure, temperature and pH value of hot spring water, and the quality and utilization of hot spring water are improved simultaneously. This process is mainly aimed at utilizing and applying hot spring systems with carbonate scaling. The formation mechanism of carbonate scaling is primarily related to the pH, temperature, pressure and salinity of hot spring water, which interact and influence each other. We first analyze the geochemical process of geothermal fluid through the stratigraphic structure, then examine the composition of scale and the cause of scaling in hot spring water through the scale components and water quality characteristics. Finally, we calculate the carbonate saturation coefficient using the Oddo-Tomson saturation Index to evaluate the scaling trend of hot spring water. On this basis, deep well pumps, heat exchangers, vacuum devices, filters and other equipment are used to control the pressure, temperature, and pH of the geothermal transport process under various working conditions to achieve the effect of scale removal and prevention. The study found that increasing the wellhead pressure and lowering the temperature can effectively prevent carbonate scaling in the pipeline network and improve the quality of hot spring water. The results showed that the outlet temperature of the wellhead can be increased by more than 20°C at the elevated pressures without observing any scaling problem. Meanwhile, the bicarbonate ion can be increased by about 30%, and the concentrations of calcium and magnesium ions in the spring stream can be increased. This work also unveiled that under the optimal combination conditions of a pH value and vacuum degree, the precipitation of calcium and magnesium ions in the pipeline can be enhanced above the ground for early scaling promotion, then leave a clear downstream spring. Water quality analysis showed that the process only influenced the reduction of sodium, strontium and bicarbonate ions in hot spring water, but had little effect on other minerals and trace elements. The new anti-scaling and descaling methods can improve the quality of hot spring water, maintain the activity, health and medical value of hot spring water, enhance the comprehensive utilization of geothermal resources, and harbor great commercial applications.

1. INTRODUCTION

Geothermal water is rich in many kinds of trace elements, and when the temperature and pressure of geothermal water change during the process of transporting it from underground to above ground, some of the mineral ions will precipitate and adhere to the geothermal wells and pipes to form scale, which will block the pipeline network system after accumulating to a certain amount. Although the methods in physical and chemical can solve the scaling of the pipe network and equipment on the well, the treatment of the well is still mainly in the mechanical descaling method today [1]. This process is simple, but often needs to shut down to descale, such as Yunnan and other places' high-temperature geothermal wells using mechanical descaling with more significant safety risks [2]. This situation arises because geothermal wells are buried deep underground, and conventional methods are difficult to apply. On the other hand, when geothermal water is used as hot springs, it is necessary to retain or enhance the characteristics of the original features of hot spring water, the popular physical and chemical solutions operated on the ground conditions are not appropriate [3].

This paper takes geothermal water in Eryuan County, Yunnan Province, as a case study. Eryuan is in the Jianchuan-Xiaoguan-Jinping high-temperature geotropic zone [2], known as the "City of Hot Springs" with abnormally active hydrothermal activities. Geothermal water is rich in metasilicic acid, strontium, lithium, fluorine, calcium and other elements, which are beneficial to the human body after bathing, so the hot spring industry in Eryuan is developing rapidly. According to the field survey and water quality analysis, the chemical type of local geothermal water is $HCO_3 \cdot SO_4$—Na·Ca type spa water, which is weakly alkaline, and the hot spring temperature is above 60℃. The temperature of underground water in Flaming Mountain areas is above 120℃. As a result of high temperature and scaling, using conventional hot water pumps at the local hot spring hotels in geothermal water above 70 ℃ could be damaged in about ten days. One solution for the local hot spring hotels is to adopt the way of adding gas and drainage to obtain geothermal water [2]. However, the well is even more intended for scaling issues (especially the outlet above 80 ℃ hot spring) due to the underground pressure relief of hot spring wells. Typically, the Eryuan's Flaming Mountain hot spring hotel needs to clean the hot spring well once every 3-5 days by mechanical knocking, and the business has to be closed for at least a couple of days during the descaling period. Meanwhile, the mechanical descaling treatment is costly and dangerous, so scaling in the well has become a significant problem for the local spa industry.

2. DETERMINATION METHOD OF SCALING TENDENCY

The scaling prediction of geothermal water in Yunnan Eryuan is determined based on the Ryznar stability index method as specified in the Geological Survey Specification for Geothermal Resources[2], calculated as follows:

Ryznar (RI) stability index

$$RI=2pHs-pHa \quad (1)$$

$$pHs=-lg[Ca^{2+}]-lg[ALK]+Ke \quad (2)$$

pHs—Calculated pH value, dimensionless.

pHa—Measured pH value, dimensionless.

$[Ca^{2+}]$—Calcium ion concentration in water, mol/l.

[ALK]—Total alkalinity (mainly refers to bicarbonate ion concentration), mol/l.

Ke—Constant (when the total solid is 200mg/l~6000mg/l, the value is 1.8~2.6).

When RI<4.0, Very strict scaling.

RI=4.0～5.0, Severe scaling.

RI=5.0～6.0, Medium scaling.

RI=6.0～7.0, Slight scaling.

RI＞7.0, No scaling.

3. PHYSICAL AND MECHANISM ANALYSIS OF SCALE

3.1 Component Analysis

The whole-rock X-ray powder crystal diffraction analysis of scale samples from the Eryuan area in Yunnan Province is shown in Table 1. The scale of hot springs in the Eryuan area is mainly the calcium carbonates, among which calcite is the primary scale in the Geothermal County and aragonite is the major scale in the Flaming Mountain area. Figs. 1 and 2 show typical crystal phase diagrams of the two scale compositions. Both calcite and aragonite are calcium carbonate scales, so this work of scaling promotion technology for hot spring water focuses on removing calcium carbonate, then purification.

Table 1. Composition of scale in Eryuan hot spring wells

Analysis report of X-ray powder crystal diffraction of whole rock				
Experimental conditions: physical DMAX-3C diffractometer, CuKa, Ni filter				
Report number	Sample no.	Test results, wt-%		
		quartz	calcite	aragonite
1	Direguo	2.23	97.77	
2	The volcano			100.00

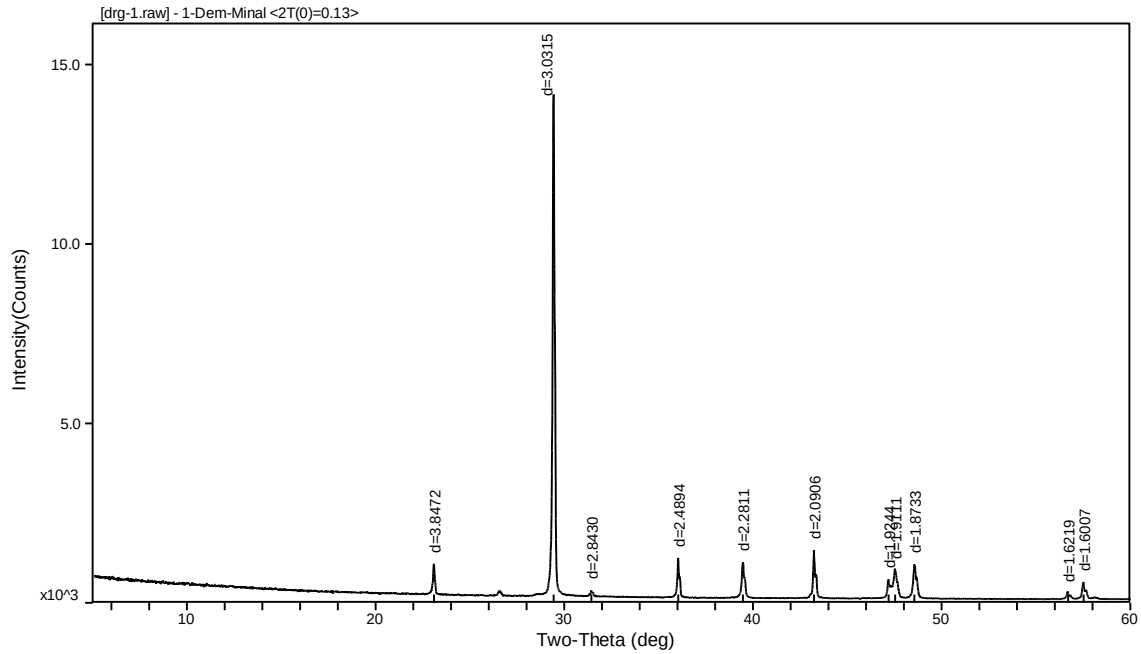


Figure 1. DAMX-3C diffraction pattern of a Geothermal County

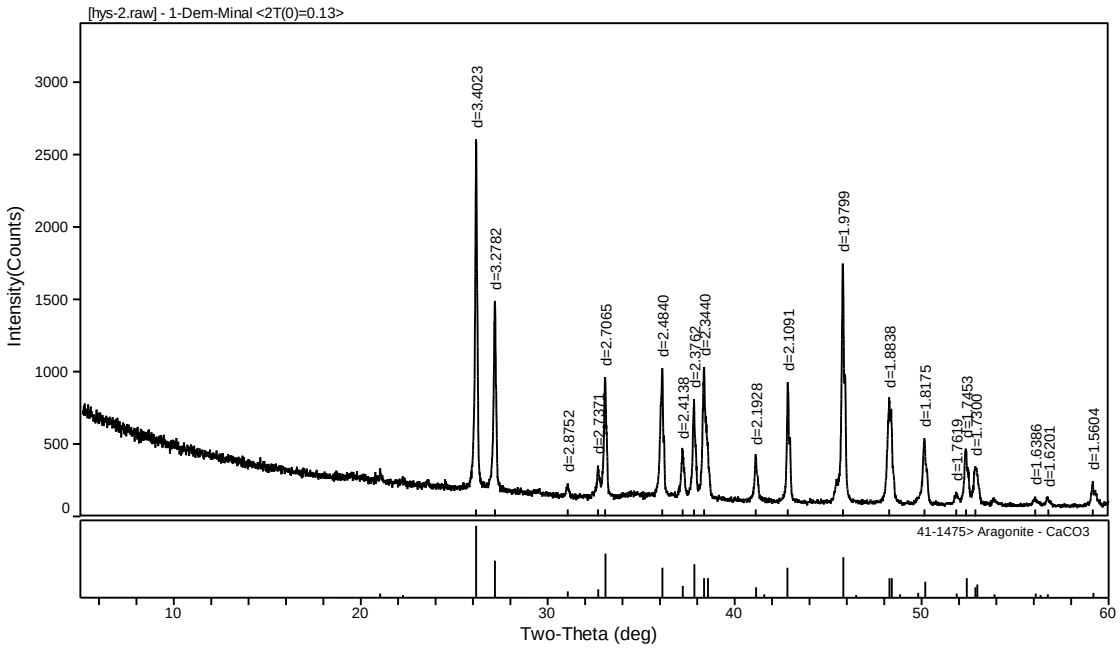


Figure 2. DAMX-3C diffraction pattern of Flaming Mountains

4. ANALYSIS OF GEOTHERMAL WATER QUALITY

Table 2 Water quality analysis table of wellhead

	Na^+ mmol/l	K^+ mmol/l	Ca^{2+} mmol/l	Mg^{2+} mmol/l	HCO_3^- mmol/l	SO_4^{2-}m mol/l	CO_3^{2-} mmol/l	F^- mmol/l	Sr^{2+} mmol/l	pH	press MPa	The wellhead temperature ℃	The downhole temperature ℃
Direguo	5.630	0.275	3.318	1.021	7.533	3.229	0	0.211	0.096	6.9	0.05	69	72
The volcano	17.200	1.404	0.051	0.140	8.398	2.714	3.459	0.395		8.78	0.02	95	121

Based on water quality test results, the Reznor (RI) stability index method calculated RI = 5.90 for the Geothermal County and RI = 7.55 for Flaming Mountains.

The Reznor (RI) stability index determines that geothermal water is of moderate scaling water quality in the Geothermal County and non-scaling water quality in the Flaming Mountain. Since the water samples were all wellhead water, the results do not apply to the downhole water.

It was determined through field visits that geothermal water in the Geothermal County area did have significant scaling, and the scaling was severe downhole in the Flaming Mountains area, with the most severely scaled geothermal wells clogging well pipes for about three days and minor scaling in the upper well pipe network. The analysis concluded that the severe downhole scaling in the Flaming Mountains area was due to the high geothermal water temperatures above 80ºC.

5. CALCIUM CARBONATE SCALING ANALYSIS

Based on whole-rock X-ray powder crystal diffraction analysis of the erogenous downhole scale, the scaling material is all calcium carbonates, and the scale types are aragonite and calcite, respectively. Brian Jones (2017) et al [1]. studied the variation of aragonite and calcite polymorphic precipitation factors with changes in temperature, pressure, pH, and dissolved elements, such as Ca, Mg, Sr, and associated gases (e.g., CO_2), while calcite is more stable than aragonite. Both aragonite and calcite are essentially calcium carbonate precipitates, which have a low solubility in water and are produced by combining calcium ions in water with carbonate or bicarbonate ions. The hydrogeochemical processes in high-temperature geothermal wells are as follows [4]:

Gas-liquid equilibrium:

$$CO_2(aq) \leftrightarrow CO_2(g) \quad (3)$$

Component equilibrium of aqueous solution:

$$HCO_3^- + H^+ \leftrightarrow CO_2(aq) + H_2O \quad (4)$$

$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^- \quad (5)$$

$$H_2O \leftrightarrow H^+ + OH^- \quad (6)$$

$$CaHCO_3^- \leftrightarrow Ca^{2+} + HCO_3^- \quad (7)$$

$$CO_3^{2-} + Ca^{2+} \leftrightarrow CaCO_3 \quad (8)$$

Finally, the solid-liquid equilibrium is:

$$CaCO_{3(S)}^0 \leftrightarrow Ca^{2+} + CO_3^{2-} \quad (9)$$

The equations above provide a more comprehensive analysis of the water quality change process for scaling in high-temperature geothermal wells, but do not consider that the reaction of OH^- with HCO_3^- at elevated pH also promotes calcium carbonate scale formation, with the following response:

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \quad (10)$$

In a typical calcium bicarbonate hot spring well, Eqs. (8) and (10) are the main processes leading to wellhead scaling due to calcium carbonate scaling precipitation. At progressively lower pressure in geothermal water, CO_2 and H_2O escape in gaseous form, so the reaction of Eq. (3) proceeds again. In an aqueous solution, due to the reduction of CO_2（aq), hydrogen ion concentration decreases, hydroxide ion concentration increases, solution pH increases, reactions (4) - (8) and (10) proceed to the right, promoting $CaCO_3$ formation. Due to the low solubility of $CaCO_3$ in solid-liquid equilibrium, it is unlikely to become an ionic state. As above reaction (9), $CaCO_3$ ionization is less, so most of $CaCO_3$ is precipitated and scaled. Take Flaming Mountain's high-temperature geothermal well as an example, the groundwater temperature is at 121°C . The pressure gradually decreases from the well to the surface. When it reaches the steam flash, the vapor mixing phenomenon occurs, and CO_2 escapes with the water vapor, leading to the CO_2 partial pressure in the geothermal water continuously decreasing, which is more favorable to calcium carbonate generation, and the scaling trend has been increasing. On the contrary, by increasing the pressure in the pipeline in the geothermal well, the flash can be elevated to the upper position of the well, preventing the phenomenon of vapor-water mixing under the well and achieving the stagnation of carbonate scale precipitation.

According to the analysis of water characteristics from Yunnan Flaming Mountain and Geothermal County, the Flaming Mountain area belongs to geothermal wells with high downhole temperature, and the downhole geothermal water is above 120℃, with severe scaling, which is in line with the appeal of high-temperature geothermal well scaling principle. The Geothermal County area has relatively low temperatures, and pH is also below 7.0, the scaling is not severe in the well until it reaches the above ground. The concentration of calcium and magnesium ions is high enough to prevent scaling, which is in line with the saturation index to judge the scaling trend of Geothermal County. Finding similar geothermal wells in the literature can help understand the principle analysis of calcium carbonate scaling in geothermal wells in Yunnan Eryuan and other places. Lei et al. evaluated the typical geothermal borehole calcium carbonate scaling in Yangbajin based on the coupled model, and concluded that CO2 partial pressure is a controlling factor of calcium carbonate precipitation [4]. They further explained that the changes in temperature and CO2 partial pressure supersaturated precipitation in the pipeline resulted in downhole scaling, and the scale location is 10-20 m above the flash point [4]. Li et al [5]. quantitatively evaluated that calcium carbonate scale formation in geothermal wells is mainly because of pH, that pH increase leads to a rise in CO_3^{2-} ions, $CaCO_3$ activity product. pH increase resulting from the high-temperature boiling or decompression leads to CO_2 degassing, and boiling is the main factor.

6. EXPERIMENTAL VERIFICATION

According to the analysis of calcium carbonate scaling in high-temperature geothermal wells and the summary of reference literature, as long as boiling is prevented and CO_2 partial pressure is increased to ensure that CO_2 does not escape can effectively stop high-temperature geothermal well scaling. To solve the problem of high-temperature geothermal water scaling in the Eryuan area of Yunnan province and considering that geothermal water is used as a hot spring spa for bathing and other recreational properties, increasing pH or decreasing CO_2 partial pressure can quickly promote calcium carbonate precipitation. We adopt the physical way of scale inhibition by increasing pressure in the high-temperature hot spring well underground above 60℃ in the Eryuan area. First, adopt micro-adjusting pH up to about 8.0 on the well, and then accelerate CO_2 escape by generating vacuum pressure to enhance calcium carbonate scale precipitation. Scale inhibition and scale promotion are achieved by micro-adjusting the pH and then physically regulating the pressure. This method has a low impact on water characteristics, thus ensuring that the beneficial trace elements of geothermal water are not affected and that the recreational properties of geothermal water are retained. The results are discussed in detail in the following experiments.

- Experimental reagents: sodium hydroxide (99%).
- Experimental measuring instruments: HY101 thermocouple thermometer; LTWSD-2000H handheld ultrasonic flow meter; BXS-Ca portable calcium ion meter; SIN-PH-6001 high-temperature pH detector.

- Experimental equipment: ZJ118QYB3-120/6.2 high temperature deep well pump; brazed plate heat exchanger (0.018 m^2); basket filter (filtering precision: 1.0 mm); regulating tank; pH regulating tank; cooling tower (8 t/h); bag filter (filtering precision: 0.1 μm, 0.5 μm, 1.0 μm, 2.0 μm); MO filter (filtering precision: 2.0 μm); vacuum scale promoter (200L).

6.1 Process flow description

The process is mainly divided into downhole scale inhibition and uphole enhanced scale promotion. The downhole part includes using the pressurization and scale inhibition method, the water is first delivered to the well through a high-temperature deep well pump, which is temperature resistant to 180°C and ensures that the wellhead pressure is above 0.3 MPa. By controlling the delivered water pressure, boiling the geothermal well downhole is prevented and increases the CO_2 partial pressure.

The upper part of the well includes the large particles in the water intercepted by the basket filter under pressure retention. The filter pore size is less than 1.0 mm to ensure that large particles do not block the heat exchanger at the back end. After the basket filter, a brazed plate heat exchanger is connected to lower the hot water temperature to below the boiling point under pressure retention, and the heat is removed by a cooling tower afterward. The cooled geothermal water is pressure relieved into a conditioning reservoir of 1 m^3, where water temperature, pH, calcium ion concentration, and bicarbonate ion concentration are measured. The testing geothermal water is pumped to the reaction pool, adjust the pH and measure the calcium ion concentration at the outlet end, then enters the vacuum scale promoter at different pH, negative pressure in the vacuum promoter precipitates carbon dioxide in the water, promotes the precipitation of calcium carbonate scale, detect the pH and calcium ion concentration of the outlet water, and then filter out the scale through the bag filter or membrane filter (MO).

Figure 3. Process flow chart of carbonate scale prevention and enhanced scale removal

6.2 Experimental steps

（1） Install the equipment and instrumentation according to the process before the experiment.

（2） Adjust the equipment and run it separately in stand-alone and inline operation.

（3） Take water samples at the wellhead without pressure retention and measure the temperature, pH and ion concentration of geothermal water (containing calcium, magnesium, bicarbonate, etc.) to determine the precipitation of scale by ion concentration.

（4） Pressure retaining scale inhibition and heat exchange at different pressures of 0.05, 0.1, 0.15, 0.2, 0.25 and 0.30 MPa at the wellhead, respectively, the temperature, pH and ion concentration (containing calcium, magnesium, bicarbonate, etc.) of the geothermal water exiting the heat exchanger were measured at each pressure condition, and temperature measurements verified the cooling effect of the heat exchanger, the pH was recorded, and ion concentration changes were analyzed. The changes in ion concentration confirmed whether calcium carbonate precipitates after cooling.

（5） Convey the cooled geothermal water to the vacuum scale promoter, keep it under pressure (gauge pressure) 0, -0.02, -0.04, and -0.06 MPa for a specific time duration, and measure the pH and ion concentration (containing calcium, magnesium, bicarbonate, etc.) every 20 minutes, mainly reflecting calcium carbonate precipitation through calcium ion concentration changes and carbon dioxide precipitation through pH changes.

（6） Adjust different pH values and repeat step 5 to verify the effect of pH on vacuum scale promotion.

（7） Intensive scale promotion followed by interception of scale through the filter.

6.3 Calculation of scale inhibition and scale removal

The amount of scale change was calculated from the change in calcium ion concentration.

$$M_T = M_{CaCO_3} + M_{MgCO_3} \quad (11)$$

$$M_{CaCO3} = 100\Delta C_{Ca} \bullet Q \quad (12)$$

$$M_{MgCO3} = 84\,\Delta\, C_{Mg} \bullet Q \quad (13)$$

$$Q = q \bullet t \quad (14)$$

M_T — Sum up the scale amount.

M_{CaCO3} — Calcium carbonate scale amount, g.

M_{MgCO3} — Magnesium carbonate scale quantity, g.

ΔC_{Ca} — Variation of calcium ion concentration in geothermal water at inlet and outlet of equipment, mmol/ L.

ΔC_{Mg}— Variation of magnesium ion concentration in geothermal water at the inlet and outlet of equipment, mmol/ L.

Q — Water quantity, m^3.

q — Water flow, m^3/h.

t — Treatment time, h.

7. RESULTS

Flaming Mountain downhole pressurization and scale inhibition experiment, a deep well pump took water at 3 m^3/h, maintaining the pressure of 0.15 MPa when the wellhead calcium ion concentration was elevated, according to the measuring data in Table 3, the wellhead pressure (gauge pressure) was 0, calcium ion concentration was 0.005 mmol/l, magnesium 0.002 mmol/l. When the wellhead holding pressure was at 0.15 MPa, calcium ion concentration increased to 0.805 mmol/l, and magnesium increased to 0.14 mmol/l.

Table 3. Water quality test data of pressurization and scale inhibition

Sampling spot	Wellhead (P= 0 MPa)		Wellhead (P= 0.15 MPa)	
	Ca (mmol/l)	Mg (mmol/l)	Ca (mmol/l)	Mg (mmol/l)
Huo Yan Shan	0.0005	0.0002	0.805	0.14

The calculations showed M_T=2765.8 g, or M_{CaCO3}=2413.5 g and M_{MgCO3}=352.3 g for transporting 30 m^3 of water per day, respectively, indicating that the scale production reduced by 2765.8 g through pressurized scale inhibition for 30 m^3 of water per day (approximately 92.19 g of scale per m^3 of water). Please note that the scale inhibition rate is inaccurate due to the difficulty of taking samples of downhole geothermal water and the specific shape and location of the calcium scale in the geothermal well.

The following experimental data were obtained and analyzed by doing downhole pressure retention and uphole cooling after negative pressure enhanced scale precipitation tests on high-temperature hot springs near Flaming Mountain in Eryuan, Yunnan province.

7.1 Underground pressurization scale inhibition

Fig. 4 shows the variation of calcium ion concentration of effluent water with pressure at the wellhead discharge pressure of geothermal wells. At the wellhead gauge pressure of 0, the wellhead effluent water is almost free of calcium ions. As the pressure increases, the calcium ions gradually increase, and the calcium ion concentration reaches the maximum at 0.15 MPa (gauge pressure) and tends to be stable. Through the experimental situation and data analysis, the boiling point temperature of the system increases in the case of holding pressure, the wellhead outlet water does not boil, and the amount of CO_2 production is small according to the equation (4). It is known that the CO_2 gas decreases and the amount of CO_2 in the solution increase, preventing the reaction (3) from proceeding. The pH does not increase, and calcium carbonate decreases, thus increasing the concentration of calcium ions in the outlet water.

Fig. 5 shows the variation of bicarbonate ion (HCO_3^-) concentration with gauge pressure in the wellhead outlet water. The HCO_3^- concentration increases gradually with increasing pressure, reaching the maximum at the gauge pressure of 0.15 MPa, which prevents the geothermal water from boiling at 120°C. According to equation (4), product increase can inhibit the reaction of HCO_3^- with H^+ to a greater extent, and more HCO_3^- in the effluent water can be expected.

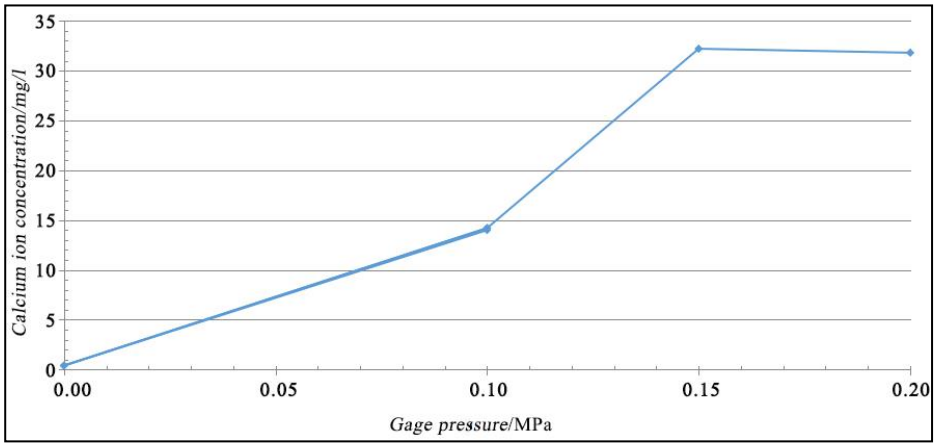


Figure 4. Variation of wellhead calcium ion concentration with pressure under different pressures

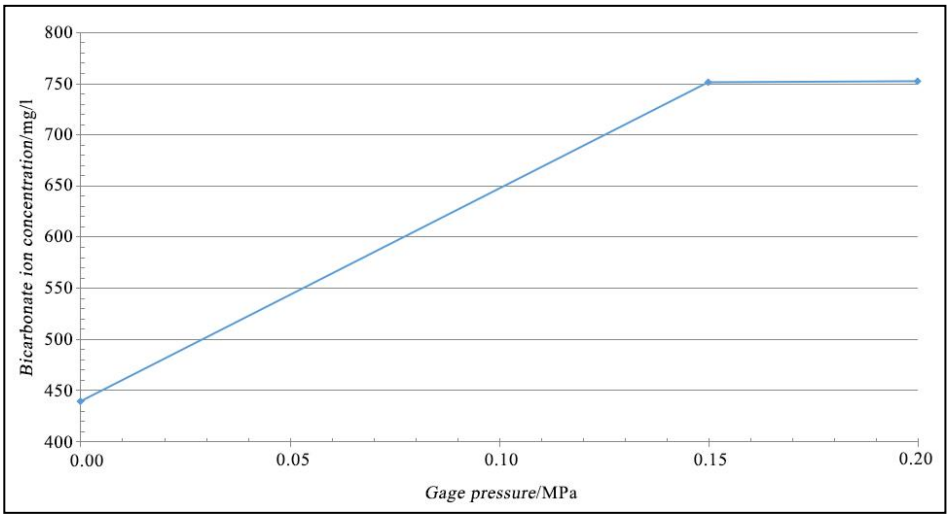


Figure 5. Changes in bicarbonate ion concentration in effluent under different pressures

Fig. 6 shows the variation of geothermal water temperature with pressure at 100 m downhole location and at the wellhead. As the pressure gradually increases, the temperature at the wellhead gradually increases and then tends to level off when the temperature increases to the same level as the bottom of the well. The equilibrium temperature at the wellhead is about 120°C, slightly lower than the downhole water temperature, which should be the temperature loss due to heat dissipation during the rise of well water. The temperature dropped slightly when the gauge pressure was raised from 0.15 MPa to 0.20 MPa, which could be an error from a slight fluctuation in the downhole geothermal water temperature and the detecting limit of the thermometer.

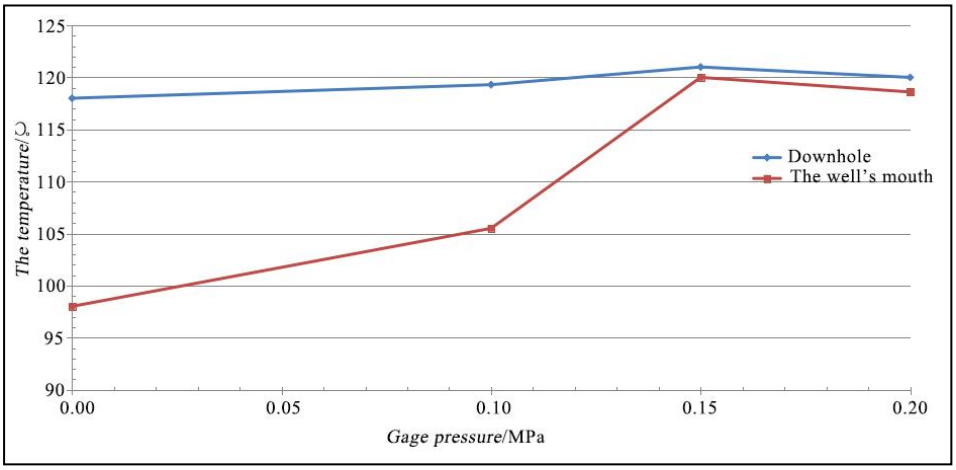


Figure 6. Variation of geothermal water temperature with pressure at 100 m downhole and wellhead

7.2 Scale promotion at negative pressure

From Fig. 7, there is no change of Ca^{2+} concentration with time when the gauge pressure remained at 0 MPa, but the Ca^{2+} concentration decreased from about 35 mg/l to 20 mg/l when the gauge pressure was adjusted to a negative pressure by vacuum, such as -0.02, -0.04 and -0.06 MPa. At the three different pressures held for 30 mins, Ca^{2+} removal rates were 29.19%, 35.43% and 43.64%, respectively. Then with continued to 60 minutes, the Ca^{2+} removal rates increased to 48.65%, 42.37% and 48.73%, respectively. It is interesting to note that Ca^{2+} concentration no longer changes after 60 mins. This is because the release of CO_2 from geothermal water under negative pressure, that is, higher CO_3^{2-} together with Ca^{2+} in the geothermal water, results in the crystallization and precipitation of $CaCO_3$ scales.

Fig. 8 shows the pH change curve under negative pressure for scale promotion. Similar to the situation above, the pH remains constant with time at 0 MPa. Once the pressure was adjusted to the negative values, such as -0.02, -0.04 and -0.06 MPa, the pH of geothermal water increased. It was due to the release of CO_2 from the sample water based on equation (4). However, the pH gradually leveled off 40 minutes later, indicating no more release and escape of CO_2.

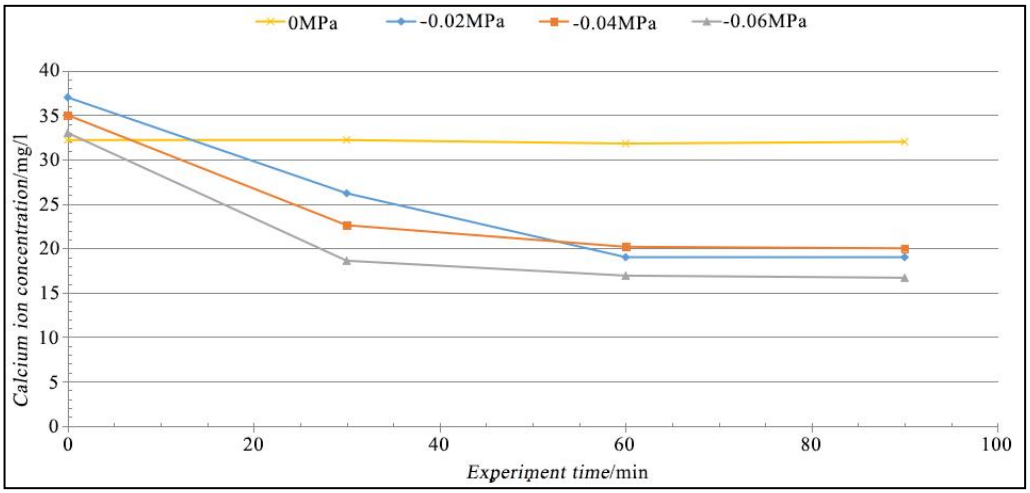


Figure 7. Change curve of calcium ion concentration with time at different vacuums (gauge pressure)

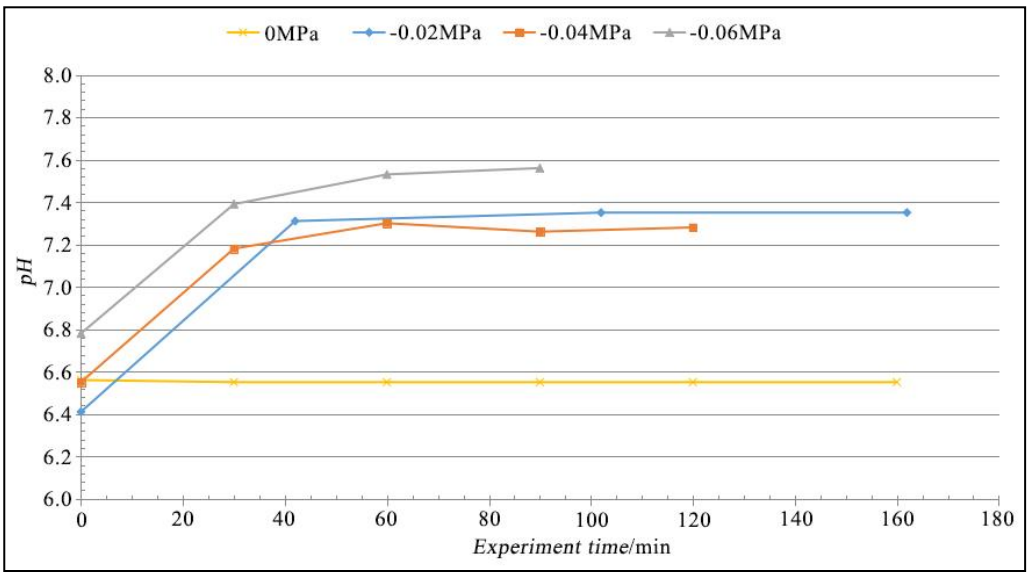


Figure 8. pH change curve of calcium ion concentration with time at -0.06 MPa (gauge pressure)

Fig. 9 shows the variation curve of calcium ions with time for different pH geothermal water under fixed negative pressure (-0.06 MPa). When the pressure is set at -0.06 MPa in the burst vacuum vessel, Ca^{2+} concentration at the pH range of 7.55-8.0 gradually decreases with time and no longer drops after 60 minutes. The Ca^{2+} removal rate is 30%-56%. As the pH increased further up to 9.0, the vacuum still had some effect on removing Ca^{2+} to a lower concentration, and the removal rate remained at 50-60%.

To confirm the effect of Ca^{2+} removal under negative pressure, we selected a high Ca ion geothermal well in the Eryuan Geothermal County area but cooled to 50°C and 40°C at negative pressure. From Fig. 10, with a comparison of the measurements at the gauge pressure of 0 MPa, both geothermal water at 40°C and 50°C were able to remove Ca at a negative pressure of 0.06 MPa. The Ca^{2+} removal rate was 9.46% and 16.89% after 30 and 60 min, respectively, for 40°C geothermal water, but reduced to 7.24% and 11.84%, respectively, for geothermal water cooled to 50°C. More Ca^{2+} is removed at 40°C.

Fig. 11 shows the pH changes as a function of time at different cooling temperatures and negative pressure. Clearly, the pH of geothermal water at both 40°C and 50°C is elevated under negative pressure, indicating that there is an escape of CO_2 from the geothermal water under negative pressure. In contrast, the pH of 50°C hot water is elevated more significantly.

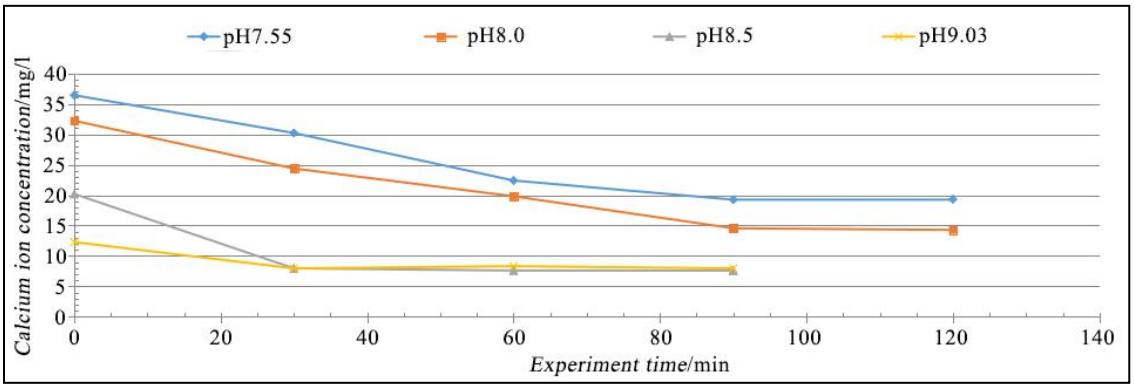


Figure 9. Change curve of calcium ion concentration with time at different pH and -0.06 MPa (gauge pressure)

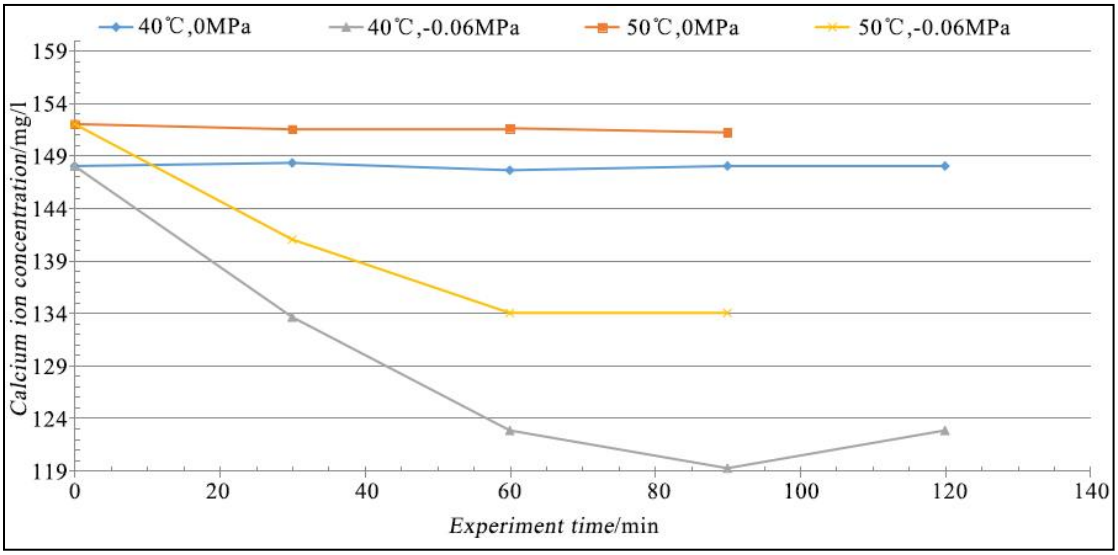


Figure 10. Ca ion concentration as a function of time at different temperatures and -0.06 MPa (gauge pressure).

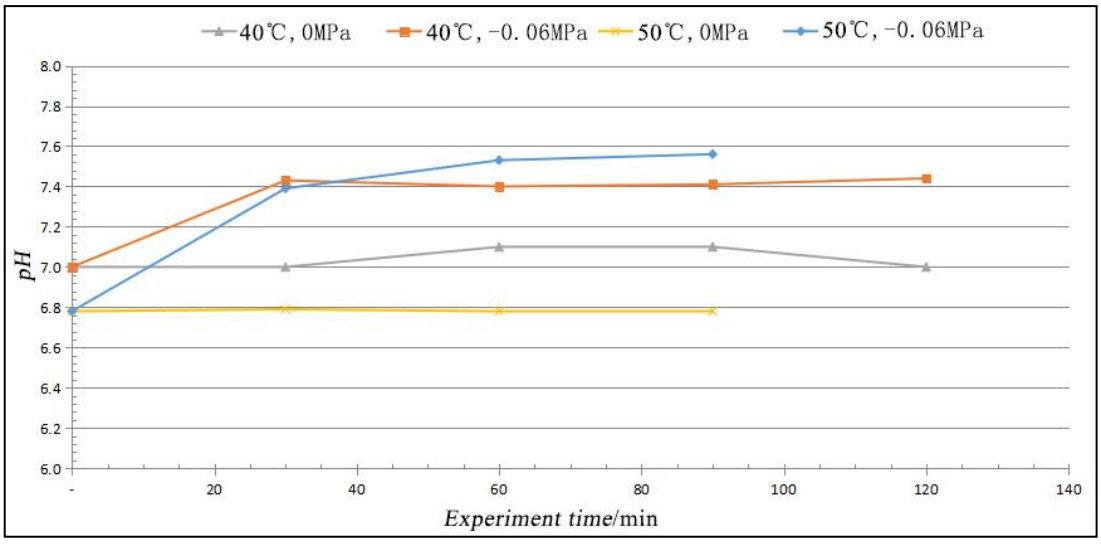


Figure 11. pH as a function of time at different temperatures and -0.06 MPa (gauge pressure)

The work in this study indicates that downhole scale inhibition can obviously prevent downhole scaling. In contrast, the precipitation is enhanced by setting negative pressure for the uphole scale. Meanwhile, it is worth noting that the actual water quality inside the well and the partial pressure of carbon dioxide before and after the process were not obtained, and the scale inhibition efficiency of the pressure increase still needs to be determined. Further tests are required in order to resolve it.

The measurements of scale promotion for the uphole well indicate that the ion concentrations of Ca^{2+} and HCO_3^-, and pH values are no longer changed after 60 minutes of maintaining negative pressure at different temperatures and pH. The results suggest that the

CO_2 and water vapor in the geothermal water can be escaped rapidly for the first 60 mins under negative pressure. Meanwhile, the pH of geothermal water is raised, and more Ca^{2+} in the water is precipitated. However, after 60 minutes, without other external factors to accelerate the release of CO_2, and thus no significant Ca^{2+} removal was observed.

7.3 Analysis of water quality for negative pressure intensification and scale promotion in geothermal countries

The results above showed decent agreement with Reznor (RI) stability index calculations. RI=6.0 for the raw geothermal water, RI=6.82 for the same water adjusted to the enhanced scale promotion testing conditions of pH=7.55 at negative pressure, and RI=6.92 under pH=8.0 at negative pressure. Based on these calculations, the raw water represents an index of moderate scaling to slight scaling. Under the enhanced scale promotion conditions, the RI values of the effluent are close to 7.0, indicating a state of non-scaling.

The experimental water samples, analyses in Tables 4-6, show that the original geothermal water type is HCO_3 •SO_4—Na •Ca type, which is changed to HCO_3 • SO_4—Na type after adjusting to the scaling promotion processing system. The calcium ion removal rate is 82.5% and 86.7% at pH= 7.55 and 8.0, respectively, and the precipitation amount of the $CaCO_3$ scale is 521.2g and 547.9g. The most effective ions are calcium ions and sodium ions. Please note that sodium ions in the testing system replaced the removed calcium ions to maintain the water balance of anions and cations. The results showed that bicarbonate and strontium are the most effective ions after calcium. The analyses showed that the bicarbonate ions were reduced by about 10-20% and strontium ions by 50%. The sample analysis confirmed that most of the bicarbonate ions were precipitated together with calcium ions in the process, and strontium ions were removed by combining with bicarbonate ions to form strontium carbonate precipitates. In addition, there is almost no effect on other ions, especially the trace elements to be beneficial to human beings in spa water, such as bicarbonate, metasilicate, lithium and zinc ions, indicating that the process has achieved the purpose of protecting the water quality of geothermal water and ensuring the recreation of hot springs.

Table 4. Raw water quality analysis

<table>
<tr><td colspan="2">The experimental configuration</td><td colspan="7">High temperature and pressure pump</td></tr>
<tr><td colspan="2">Environmental parameters</td><td colspan="7">Ambient temperature: 23-28 (C), Altitude: 2200 m</td></tr>
<tr><td colspan="2">Working condition</td><td colspan="7">Temperature: 65℃, outlet pressure: 0.1 MPa (gauge pressure)</td></tr>
<tr><td colspan="9">Testing data</td></tr>
<tr><td colspan="2" rowspan="3">project</td><td rowspan="3">ρ(B)/（mg/L）</td><td>C</td><td>x</td><td rowspan="3">project</td><td rowspan="3">ρ(B)/（mg/L）</td><td rowspan="3">project</td><td rowspan="3">ρ(B)/（mg/L）</td></tr>
<tr><td>(1/zB$^{z\pm}$)</td><td>(1/zB$^{z\pm}$)</td></tr>
<tr><td>mmol/L</td><td>%</td></tr>
<tr><td rowspan="6">cationic</td><td>K^+</td><td>11.31</td><td>0.289</td><td>1.96</td><td>Dissolved total solids</td><td>1133.93</td><td>barium</td><td>0.086</td></tr>
<tr><td>Na^+</td><td>136.10</td><td>5.920</td><td>40.09</td><td>metasilicate</td><td>61.54</td><td>chromium</td><td>< 0.02</td></tr>
<tr><td>Ca^{2+}</td><td>126.64</td><td>6.319</td><td>42.79</td><td>Free carbon dioxide</td><td>15.57</td><td>lead</td><td>< 0.01</td></tr>
<tr><td>Mg^{2+}</td><td>27.14</td><td>2.233</td><td>15.12</td><td>lithium</td><td>0.25</td><td>antimony</td><td>< 0.0001</td></tr>
<tr><td>Fe^{2+}+Fe^{3+}</td><td>0.086</td><td>0.005</td><td>0.03</td><td>strontium</td><td>10.13</td><td>manganese</td><td>< 0.01</td></tr>
<tr><td>summation</td><td>301.28</td><td>14.767</td><td>100.00</td><td>iodide</td><td>< 0.05</td><td>nickel</td><td>< 0.01</td></tr>
<tr><td rowspan="8">anionic</td><td>HCO_3^-</td><td>448.86</td><td>7.356</td><td>51.61</td><td>zinc</td><td>0.022</td><td>cobalt</td><td>< 0.005</td></tr>
<tr><td>CO_3^{2-}</td><td>0.00</td><td>0.000</td><td>0.00</td><td>selenium</td><td>< 0.0005</td><td>vanadium</td><td>< 0.005</td></tr>
<tr><td>Cl^-</td><td>14.81</td><td>0.418</td><td>2.93</td><td>copper</td><td>< 0.01</td><td>aluminum</td><td>< 0.05</td></tr>
<tr><td>SO_4^{2-}</td><td>287.50</td><td>5.986</td><td>41.99</td><td>arsenic</td><td>0.022</td><td>silver</td><td>< 0.01</td></tr>
<tr><td>F^-</td><td>9.00</td><td>0.474</td><td>3.32</td><td>mercury</td><td>< 0.0001</td><td>Volatile phenol</td><td>-</td></tr>
<tr><td>NO_3^-</td><td>1.29</td><td>0.021</td><td>0.15</td><td>cadmium</td><td>< 0.0004</td><td>cyanide</td><td>-</td></tr>
<tr><td rowspan="2">summation</td><td rowspan="2">761.46</td><td rowspan="2">14.254</td><td rowspan="2">100.00</td><td>borate</td><td>0.30</td><td>nitrite</td><td>< 0.003</td></tr>
<tr><td>bromide</td><td>0.060</td><td>bromate</td><td>-</td></tr>
<tr><td colspan="2">Nothing visible to the naked eye</td><td colspan="3"></td><td colspan="2">Coliform - MPN/100mL</td><td colspan="2">The oxygen consumption of 0.96 mg/L</td></tr>
<tr><td colspan="2">Chromaticity < 5</td><td colspan="3">Total hardness (in $CaCO_3$) 428.02 mg/L</td><td colspan="2">Streptococcus faecalis - CFU/250mL</td><td colspan="2">Anion synthetic detergent - mg/L</td></tr>
<tr><td colspan="2">Turbidity < 1</td><td colspan="3">Total alkalinity (in $CaCO_3$) 319.02 mg/L</td><td colspan="2">Pseudomonas aeruginosa - CFU/250mL</td><td colspan="2">Mineral oil - mg/L</td></tr>
</table>

No odor and taste	Total acidity (in $CaCO_3$) 17.71 mg/L	Clostridium perfringens - CFU/50mL	Radium - 226 Bq/L
PH 6.86			Total beta Bq/L
Note: ρ(B)/ (mg/L): density of substance B in milligrams per liter; C($1/zB^{z\pm}$): quantity solubility of substance; x($1/zB^{z\pm}$): content percentage; "-": indicates not tested.			

Table 5. Enhanced descaling experiment effluent water quality at pH=7.55 negative pressure

The experimental configuration		High temperature and pressure pump + basket filter + heat exchange + regulating water tank +pH adjustment + vacuum cleaner + bag filter						
Environmental parameters		Ambient temperature: 23-28 (C); Altitude: 2200 m						
Working condition		Experimental temperature: 60℃, pH: 7.55, experimental pressure: -0.06 MPa, Pressure holding time: 60 minutes, experimental water volume: 1 m^3.						
Testing data								
project		ρ(B)/（mg/L）	C ($1/zB^{z\pm}$) mmol/L	x ($1/zB^{z\pm}$) %	project	ρ(B)/（mg/L）	project	ρ(B)/（mg/L）
cationic	K^+	11.90	0.304	2.16	dissolved total solids	1155.00	barium	0.028
	Na^+	247.95	10.786	76.64	metasilicate	65.32	chromium	< 0.02
	Ca^{2+}	7.19	1.107	7.87	free carbon dioxide	5.19	lead	< 0.01
	Mg^{2+}	22.74	1.871	13.30	lithium	0.27	antimony	0.0012
	Fe^{2+}+Fe^{3+}	0.080	0.004	0.03	strontium	4.73	manganese	< 0.01
	summation	304.860	14.073	100.00	iodide	< 0.05	nickel	< 0.01
anionic	HCO_3^-	389.01	6.375	47.26	zinc	0.002	cobalt	< 0.005
	CO_3^{2-}	0.00	0.000	0.00	selenium	< 0.0005	vanadium	< 0.005
	Cl^-	19.26	0.543	4.03	copper	< 0.01	aluminum	< 0.05
	SO_4^{2-}	292.24	6.085	45.10	arsenic	0.032	silver	< 0.01
	F^-	9.00	0.474	3.51	mercury	< 0.0001	volatile phenol	-
	NO_3^-	0.86	0.014	0.10	cadmium	< 0.0004	cyanide	-
	summation	710.37	13.491	100.00	borate	0.33	nitrite	< 0.003
					bromide	0.059	bromate	-
Nothing visible to the naked eye					Coliform - MPN/100mL		The oxygen consumption of 1.12 mg/L	
Chromaticity < 5		Total hardness ($CaCO_3$)149.04mg/L			Streptococcus faecalis - CFU/250mL		Anion synthetic detergent - mg/L	
Turbidity < 1		The total alkalinity (in $CaCO_3$) was 319.02mg/L			Pseudomonas aeruginosa - CFU/250mL		Mineral oil - mg/L	
No odor and taste		Total acidity (in $CaCO_3$) 5.90 mg/L			Clostridium perfringens - CFU/50mL		Radium - 226 Bq/L	
PH 8.08							Total beta Bq/L	
Note: ρ(B)/ (mg/L): density of substance B in milligrams per liter; C($1/zB^{z\pm}$): quantity solubility of substance; x($1/zB^{z\pm}$): content percentage; "-": indicates not tested.								

Table 6. Enhanced descaling experiment effluent water quality at pH=8 negative pressure

The experimental configuration	High temperature and pressure pump + basket filter + heat exchange + regulating water tank +pH adjustment + vacuum cleaner + bag filter

Environmental parameters		Ambient temperature: 23-28 (℃); Altitude: 2200 m						
Working condition		Experimental temperature: 60℃, pH: 8.0, pressure: -0.06 MPa, Pressure holding time: 60 minutes, experimental water volume: 1 m^3.						
Testing data								
project		ρ(B)/（mg/L）	C ($1/zB^{z\pm}$) mmol/L	x ($1/zB^{z\pm}$) %	project	ρ(B)/（mg/L）	project	ρ(B)/（mg/L）
cationic	K^+	11.54	0.295	2.22	dissolved total solids	1208.04	barium	0.032
	Na^+	234.35	10.194	76.76	metasilicate	62.97	chromium	< 0.02
	Ca^{2+}	16.83	0.840	6.32	free carbon dioxide	0.00	lead	< 0.01
	Mg^{2+}	23.66	1.947	14.66	lithium	0.26	antimony	0.0012
	Fe^{2+}+Fe^{3+}	0.082	0.005	0.03	strontium	5.54	manganese	< 0.01
	summation	286.46	13.281	100.00	iodide	< 0.05	nickel	< 0.01
anionic	HCO_3^-	353.09	5.787	42.22	zinc	0.004	cobalt	< 0.005
	CO_3^{2-}	29.43	0.981	7.16	selenium	< 0.0005	vanadium	< 0.005
	Cl^-	14.81	0.418	3.05	copper	< 0.01	aluminum	< 0.05
	SO_4^{2-}	289.77	6.033	44.02	arsenic	0.040	silver	< 0.01
	F^-	9.00	0.474	3.46	mercury	< 0.0001	volatile phenol	-
	NO_3^-	0.90	0.015	0.11	cadmium	< 0.0004	cyanide	-
	summation	697.00	13.706	100.00	borate	0.34	nitrite	< 0.003
					bromide	0.059	bromate	-
Nothing visible to the naked eye					Coliform - MPN/100mL		The oxygen consumption of 0.63 mg/L	
Chromaticity < 5		Total hardness (in $CaCO_3$) 139.49 mg/L			Streptococcus faecalis - CFU/250mL		Anion synthetic detergent - mg/L	
Turbidity < 1		Total alkalinity (in $CaCO_3$) 314.11 mg/L			Pseudomonas aeruginosa - CFU/250mL		Mineral oil - mg/L	
No odor and taste		Total acidity (in $CaCO_3$) 0.00 mg/L			Clostridium perfringens - CFU/50mL		Radium - 226 Bq/L	
PH 8.61							Total beta Bq/L	
Note: ρ(B)/ (mg/L): density of substance B in milligrams per liter; C($1/zB^{z\pm}$): quantity solubility of substance; x($1/zB^{z\pm}$): content percentage; "-": indicates not tested.								

8. CONCLUSIONS

Under the actual situation of geothermal water in Eryuan, Yunnan province, this research study developed several new approaches of scale inhibition and scale promotion technology, which can prevent the scaling of downhole and uphole transmission pipe networks. In addition, the methods also increased the spa water's temperature and the ion concentrations of beneficial elements (mainly bicarbonate ions and trace elements).

The main findings are as follows:

- Using a high-temperature and high-pressure pump in the well above 120℃, maintain the wellhead outlet pressure up to 0.2 MPa, the hot water in the lifting pipe is held for the non-boiling state, reducing the generations of carbon dioxide and water vapor to prevent calcium carbonate scale precipitation. At the same time, it can increase the water temperature and the concentration of calcium and bicarbonate ions at the outlet, leading to lower energy consumption from steam vaporization. Therefore, the improvement of spa water quality can be achieved. Experiments have shown that the high-temperature geothermal water in the Eryuan area of Yunnan province can reduce 92.19 g of calcium carbonate scale per cubic of water after pressurization.

- Adjusting the geothermal water to a negative pressure in the ground network can promote the precipitation of calcium carbonate scale and lower the calcium ions in the spa water. The calcium ion concentration can continuously be removed within the first 60 minutes at pH below 8.0 and negative pressure of 0.06 MPa (gauge pressure), and the calcium ion removal rates are about 50%-60%.

- The geothermal water treatments used in this work can convert the spring type from HCO_3 • SO_4—Na • Ca type to HCO_3 • SO_4—Na type geothermal water, and the Reznor (RI) stability index calculation confirms the moderate scaling index for the raw water to slight scaling index for the treated water. In contrast, a method for scale promotion on the ground has great potential to prevent the scale formation of back-end pipe networks and equipment. In addition, the processing system can remain the most beneficial ions (such as sulfate, metasilicate, lithium, zinc, etc.) in the spa water from change, except for reducing bicarbonate ions by 10-20% and strontium ions by about 50%.

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